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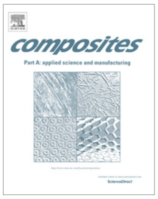

Phosphorylated cellulose applied for the exfoliation of LDH: An advanced reinforcement for polyvinyl alcohol

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ABSTRACT

Phosphorylated cellulose was used as a bio-based anion surfactant to exfoliate layered double hydroxides (PC-LDHs). The X-ray diffraction results showed that the interlayer spacing distances are significantly enlarged after intercalated by phosphorylated cellulose. TEM images showed that LDHs are successfully synthesized and distributed along the cellulose chains. The modified LDH was used as a reinforcement for polyvinyl alcohol. The thermal stability of PVA composites is improved after the addition of PC-LDH. In addition, the flame retardancy of PVA composites were significantly improved with the combination of PC-LDH, peak heat release rate (PHRR) was reduced. Meanwhile, the total heat release (THR) was also decreased. Moreover, the tensile strength of the polyvinyl alcohol was simultaneously improved by the increase of the loading. This work extended the application of cellulose and provide solution for enhancement of materials.

1. Introduction

During the past decades, the renewable and biodegradable materials have attracted considerable interests due to the environment concerns and realization of gradual depletion of fossil resources. As a natural non-toxic polysaccharide, cellulose is one of the most abundant and relatively inexpensive sustainable polymers [1]. However less than 2% is recovered for utilization and the majority is primarily burned [2]. The structure of cellulose is made of sugar rings linked by glycosidic bonds and side group (hydroxyl), which can directly affect the polysaccharide's charge density and chemical reactivity [3]. As reported, the OH groups of PVA can form strong hydrogen bonds with the ring oxygen of cellulose, which can improve its mechanical property [4].

Poly(vinyl alcohol) (PVA) is one of the most popular materials for membrane and coating materials, due to its high chemical resistance, biodegradability, good performance in respect of mechanical behavior and excellent optical property for example [5–7]. Even so, PVA like many other polymers, has the character of easier flammability, thereby restricting its application in fields in which fire safety is paramount [8,9]. So it is of great significance to improve the flame retardancy of PVA and extend its application. Many research works have been done to retard the flammability of PVA in recent years. Most of them are related to the halogen-containing compounds, which can effectively improve the flame retardancy of PVA [10,11]. However, the addition of these halogen-containing compounds may cause the evolution of harmful gases, corrosive smoke and pollution of environment, so a high-efficiency halogen-free flame retardant system for PVA is desirable.

Polymer/inorganic hybrids have been the common concerns of researchers due to their unique structures and enhanced properties [12,13]. Layered structure materials, such as LDHs, have received particular attention due to their unique properties, which can be dramatically improved after exfoliation. LDHs are one of anionic layered organic materials with exchangeable anions between the layer spaces [14] and can be easily tailored during synthesis process due to their structural homogeneity and composition. In previous work, LDHs have shown promising potential for the improvement of flame retardancy [15–18]. It is well known that the flame retardancy of polymer/inorganic hybrids is depended on the dispersion of inorganic in polymers [19]. Indeed, the intercalation process of LDHs is hard to achieve due to the high surface charge density and difficulty of ion exchange [20]. After several years of efforts by many researchers, several materials, such as polyacrylamide [21], sodium dodecyl benzene sulfonate

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[22] and etc. [23,24], have been used as the anion surfactants. Even so, bio-based anion surfactant is rarely reported. On the other side, the incorporation of inorganic materials may cause the decline in mechanical properties due to the decrease of interface interactions between polymers and inorganic materials. Therefore, it is an issue that how to both improve the flame retardancy and mechanical property of PVA.

In this work, a facile and green method to prepare the phosphorylated cellulose (PC) modified LDH (PC-LDH) was produced and the resultant PC-LDH was used as a reinforcement to improve the flame retardancy and tensile strength of PVA. Cellulose was firstly used as an anion surfactant to enlarge the interlayer spacing distance of LDH after phosphorylated process. The resulted PC and PC-LDH were characterized by TEM, FTIR, XRD and XPS. The thermal stability of LDH was improved by the introduction of PC. The flame retardancy of PVA composites was evaluated by micro-combustion calorimeter. Moreover, the tensile strength of PC-LDH based PVA is also investigated.

2. Experimental section

2.1. Raw materials

Microcrystalline cellulose (Avicel PH101, particle diameter, 20–100 μm, molecular weight: about 36,000) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ethanol, phosphorous acid, sodium hydroxide (NaOH), urea, aluminium nitrate ($Al(NO_3)_3{\cdot}9H_2O$) and nickel nitrate ($NiNO_3{\cdot}6H_2O$) were received from Changzheng Chemical Reagent Corp. PVA (polymerization degree: 1750 ± 50, hydrolysis: 87–89%, CP) is purchased from Sinopharm Chemical Reagent Co. Ltd.(Shanghai, China).

2.2. Preparation of phosphorylated cellulose (PC) and phosphorylated cellulose intercalated layered double hydroxides (PC-LDH)

Phosphorylated cellulose [24] was synthesized by the reaction of microcrystalline cellulose with phosphorous acid in molten urea. Urea (12.48 g) was added into a 250 mL, three-necked flask under constantly stirring, and heated at 140 °C and flushed with nitrogen. Microcrystalline cellulose (2 g) and phosphorous acid (10.28 g) were added and maintained at 150 °C for 5 h. Then, the reacted mixture was dissolved in 1 M aqueous NaOH and precipitated with ethanol. The process was repeated at least three times. Furthermore, the mixture was purified by diafiltration overnight. Then, the phosphorylated cellulose solution could be obtained [3].

The synthesis of PC-LDH is according to a simple co-precipitation method [25]. Typically, the phosphorylated cellulose solution ($10\ g\ L^{-1}$) was stirred in a 500 mL, three-necked flask, by adjusting the pH value to 10 with 1 M aqueous NaOH. Then, 4.64 g of $NiNO_3{\cdot}6H_2O$ and 3.0 g of $Al(NO_3)_3{\cdot}9H_2O$ were dissolved in 150 mL of deionized water completely and was added into the PC solution, accompanied by maintaining the pH value at 10 using 1 M NaOH aqueous. After the finish of dripping, the reaction temperature was adjusted to 75 °C for 24 h. The resulting precipitation was collected and washed by deionized water for several times, then dried at 60 °C overnight. The synthesis of LDH was also according to the similar procedure: 4.64 g of $NiNO_3{\cdot}6H_2O$ and 3.0 g of $Al(NO_3)_3{\cdot}9H_2O$ were dissolved in 150 mL of deionized water completely and the pH value was maintained at 10 using 1 M NaOH aq. Then, the reaction temperature adjusted to 75 °C for 24 h. The products was washed by deionized water for several times, then dried at 60 °C overnight.

2.3. Preparation of PVA and its composites film

4.9 g of PVA was dissolved in 50 mL deionized water at 95 °C in a three-neck flask with mechanical stirring to form an aqueous solution [26]. Then, 0.1 g of PC-LDH was added into the above solution under stirring and ultrasonication treatment for 30 min. Then, the mixture was further stirred for 24 h. Finally, the mixture was cast onto glass plates and dried at 40 °C in an oven for 2 days to form flat films which were peeled off and further heated at 80 °C for 1 day to remove residual water. The above sample with a 2% loading was marked as PVA-PC-LDH2. And other samples was marked as PVA0, PVA-LDH2, PVA-PC-LDH0.5 and PVA-PC-LDH1. The pure sample and other composites were prepared by the same method. The film were cut into certain species for further measurements.

2.4. Characterization

X-ray diffraction (XRD) measurements was performed with a Japan Rigaku D = Max – Ra rotating anode X-ray diffractometer equipped with a Cu Ka tube and Ni filter ($\lambda = 0.1542$ nm).

Transmission electron microscopy (TEM) images were obtained on a Jeol JEM-100SX transmission electron microscope with an acceleration voltage of 100 kV.

The thermogravimetric analysis (TGA) of samples was undertaken using TGA-Q5000 apparatus (TA Co., USA) from 50 °C to 700 °C at a heating rate of $20\ °C\ min^{-1}$. The weight of all samples was maintained within 3–5 mg in an open platinum pan.

X-ray photoelectron spectroscopy (XPS) was performed on a VG Escalab Mark II spectrometer (Thermo-VG Scientific Ltd. UK), using Al Kα excitation radiation ($h\upsilon = 1486.6$ eV).

A micro-combustion calorimeter (MCC, GOVMARK) was used to evaluate the combustion properties of the samples according to ASTM D 7309-07. Samples of 4–6 mg were heated in nitrogen atmosphere at a constant heating rate 1 °C/s from room temperature to 650 °C. The decomposition products were mixed with 20 mL/min oxygen and then burned in the combustion furnace at 900 °C.

The transmittance of 1.5 mm thick PVA and its composites were measured using a UV–Vis-Spectrometer (UV-240).

The tensile strength and elongation at break were measured according to the Chinese standard method (GB 13022-91) with a WD-20D electronic universal testing instrument (Changchun Intelligent Instrument Co., Ltd., China) at a crosshead speed of $50\ mm\ min^{-1}$. The dimensions of specimens is 20 mm × 4 mm × specified thickness (Lo × b × d), the specified thickness is measured by Vernier caliper.

3. Results and discussions

3.1. Characterization of PC, LDH and PC-LDH hybrids

In Fig. 1a, XRD patterns of both pristine NiAl-LDH and PC-LDH show the two-dimensional hydrotalcite-like characteristic reflections of (003) and (006) peaks, indicative of a hexagonal lattice and R3m symmetry [27]. After calculation, the basal spacing value (d_{003}) of pristine LDH is approximately 0.76 nm, consistent with that of nitrate-intercalated LDH materials [28]. In the case of the PC-LDH hybrid, the position of basal reflections was shifted towards higher d value representing the expansion in the interlayer distance [28]. The d_{003} in the XRD pattern of PC-LDH has shifted to 4.5° with an interlayer distance of 2.01 nm, illustrating that the interlayer spaces are enlarged after the anion exchange [19]. Hence the XRD results indicate that the phosphorylated cellulose are successfully intercalated into the LDH galleries.